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Crystal engineering using polyphenols. Host–guest behaviour of planar ribbons in *C*-methylcalix[4]resorcinarene–4,4′-trimethylenedipyridine–methanol (1/2/0.5), and capture of 2,2′-bipyridyl molecules by paired calixarene bowls in *C*-methylcalix[4]-resorcinarene-2,2′-bipyridyl–methanol–water (1/1/1/1.16)

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Co-crystallisation of the *rccc* isomer of *C*-methylcalix[4]resorcinarene **1** with 4,4′-trimethylenedipyridine from methanol yields a solvated 1 : 2 adduct **2** in which the resorcinarene acts as a quadruple donor and the dipyridines both act as double acceptors, in O–H···N hydrogen bonds. The supramolecular structure consists of linear and nearly planar ribbons with the bowls of the resorcinarene units in one ribbon acting as hosts towards the -$(CH_2)_3$-spacer units of a neighbouring ribbon, acting as guests. Co-crystallisation of the same resorcinarene **1** with 2,2′-bipyridyl yields a doubly solvated 1 : 1 adduct resorcinarene–2,2′-bipyridyl–methanol–water (1/1/1/1.16) **3**. The resorcinarene, methanol and water molecules combine by means of multiple O–H···O hydrogen bonds to form paired, essentially-planar two-dimensional nets in which centrosymmetric pairs of resorcinarene bowls act as self-assembled carcerands to form large cavities in which pairs of 2,2′-bipyridyl molecules are held by a combination of O–H···N and C–H···O hydrogen bonds.

The design and construction of self-assembled microporous molecular solids is an attractive target in crystal engineering. One approach which has proved successful for the formation of structures containing isolated linear channels formed by the self-assembly of small molecular building blocks, *via* hydrogen-bond formation, is the construction of cyclic fragments which can then be induced to stack, in register, to form the channels. Thus 4,4′-sulfonyldiphenol, $O_2S(C_6H_4OH)_2$, and piperazine form such a channel structure when co-crystallised from either methanol or acetonitrile: pairs of phenolate anions $[HOC_6H_4SO_2C_6H_4O]^-$ form hydrogen-bonded $R_2^2(24)$ rings[1,2]† which are bound into parallel linear stacks by piperazinium dications $[C_4H_{12}N_2]^{2+}$. Within each stack there is a channel of cross-sectional area *ca.* 14 Å^2, too small to accommodate methanol molecules but large enough to hold acetonitrile molecules.[3] The use of this approach for the formation of wider channels requires the construction of larger rings, and we have reported the formation of nets of $R_4^4(32)$ rings in pure $O_2S(C_6H_4OH)_2$,[4] of $R_4^4(40)$ rings in $[Fe(C_5H_4COC_6H_4OH)_2]$,[5] and of $R_6^6(48)$ rings in $CH_3C(C_6H_4OH)_3/(CH_2)_6N_4$ (1/1),[6] while nets of $R_{12}^{12}(126)$ rings are formed in $CH_3C(C_6H_4OH)_3/NC_5H_4C_5H_4N$ (2/3).[7] However, in all these examples the nets are interwoven, with the interweaving characterised by differing degrees of complexity, ranging from pairwise {4, 2, 1}[8] interweaving of the nets in $O_2S(C_6H_4OH)_2$ and $CH_3C(C_6H_4OH)_3/(CH_2)_6N_4$ *via* {10,10,9} interweaving in $CH_3C(C_6H_4OH)_3/NC_5H_4C_5H_4N$ to continuous {2, ∞, 1} interweaving in $[Fe(C_5H_4COC_6H_4OH)_2]$. Such interweaving arises because the reticulations in the nets are large compared with the effective diameters of the molecular strands forming the nets. To prevent interweaving in supramolecular systems containing large rings, it is necessary to increase the thickness of the strands relative to the hole size; this principle has been demonstrated in 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl) butane/$(CH_2)_6N_4$ (1/1), where the nets contain alternating $R_6^6(40)$ and $R_6^6(60)$ rings, but are not interwoven because of the presence of the *tert*-butyl groups in the tris-phenol.[9]

Seeking to develop further the use of large and sterically-demanding molecular building blocks, we have turned our attention to polyhydroxylated calixarenes, specifically those derived from resorcinol, **1**. In general, two isomeric forms of *C*-alkylcalix[4]resorcinarenes can be obtained, a C_{4v} (*rccc* or crown[10,11]) isomer, **1a**, and a C_{2h} (*rctt* or chair) isomer, **1b**, but despite this structural versatility and the ease of synthesis, rather little use of such compounds has hitherto been made in crystal engineering. *C*-Methylcalix[4]resorcinarene, **1a** with R = Me (2,8,14,20-tetramethylpentacyclo[$19.3.1.1^{3,7}.1^{9,13}.1^{15,19}$]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaen-4,6,10,12,16,18,22,24-octol, $C_{32}H_{32}O_8$), has been shown[12] to form a 1 : 2 hydrogen-bonded adduct with 4,4′-bipyridyl which entraps acetonitrile, but the gross supramolecular structure in this product does not exploit the hydrophobic nature of the calixarene bowl.

We have now studied the solid-state adducts, **2** and **3** respectively, of this same *C*-methylcalix[4]resorcinarene with both an extended-reach bipyridyl, 4,4′-trimethylenedipyridine and with 2,2′-bipyridyl. We reasoned that addition of an aliphatic spacer group between the pyridine units in 4,4′-bipyridyl would lead to chain-formation in **2** of a type similar to that formed by 4,4′-bipyridyl itself,[12] but that additionally the C–H···π(arene) interactions between the trimethylene

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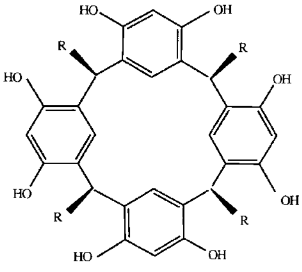
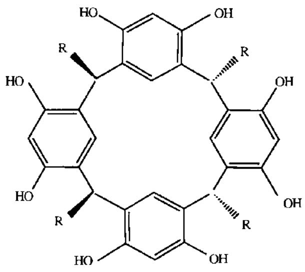
†Pattern designators[1,2] for graph sets are of the general type $G_d^a(r)$; the descriptor G may be C (chain), D (dimer, or other finite set), R (ring), or S (self) (*i.e.* an intramolecular hydrogen bond). The degree *r* represents the total number of atoms in a ring or in the repeating unit of a chain, the superscript *a* indicates the number of hydrogen-bond acceptors and the subscript *d* indicates the number of hydrogen-bond donors. Thus, for example, the hydrogen-bond pattern in the familiar carboxylic acid dimer is represented as $R_2^2(8)$.



1a



1b

spacer units in one chain and the calixarene bowls of neighbouring chains could be sufficient to control the mutual arrangement of the chains of **2** in the solid state. Similarly, with 2,2′-bipyridyl in compound **3**, we reasoned that the location of the hydrogen-bond acceptor sites in the bipyridyl would preclude the formation of a simple chain motif, possibly leading to a two- or three-dimensional system instead, resulting from some alternative mode of linkage of neighbouring resorcinarene units by the bipyridyl molecules.

Experimental

The C_{4v} isomer of *C*-methylcalix[4]resorcinarene **1a** was prepared by the literature method.[13] Repeated attempts to recrystallise this compound from methanol or from aqueous methanol invariably provided microcrystalline or powdery material for which microanalysis and ^{1}H NMR consistently indicated 6–8 molecules of water per calixarene unit. Co-crystallisation of this resorcinarene with either 4,4′-trimethylenedipyridine or 2,2′-bipyridyl from methanol solutions yielded **2** and **3** respectively, regardless of the molar ratio of resorcinarene to dipyridine originally taken, within the range of 1:1 to 1:4. Analysis for **2**, resorcinarene·4,4′-trimethylenedipyridine·MeOH (1/2/0.5): found C, 73.5; H, 6.6; N, 5.6%; $C_{58.5}H_{62}N_4O_{8.5}$ requires C, 73.4; H 6.5; N, 5.8%; for **3**, resorcinarene·2,2′-bipyridyl·MeOH·H_2O (1/1/1/1.16): found C, 68.6; H, 6.3; N, 3.7%; $C_{43}H_{46.32}N_2O_{10.16}$ requires C, 68.5; H, 6.2; N, 3.7%. Crystallisation of the resorcinarene from neat pyridine at room temperature yielded the 1:4 adduct **4** (Found: C, 72.0; H, 6.2; N, 6.4%; $C_{52}H_{52}N_4O_8$ requires C, 72.5; H, 6.1; N, 6.5%), while co-crystallisation with 4,4′-bipyridyl from solutions in either methanol or ethanol, with input molar ratios of resorcinarene to bipyridyl in the range 1:1 to 1:4, consistently yielded a microcrystalline material **5** of composition resorcinarene:bipyridyl:water (1/2/3) (Found C, 68.3; H, 5.8; N, 6.0%: $C_{52}H_{54}N_4O_{11}$ requires C, 68.5; H, 6.0; N, 6.2%).

X-Ray crystallography

Crystals of compounds **2** and **3** suitable for single-crystal X-ray diffraction were selected directly from the analytical samples. Details of the X-ray experimental conditions, cell data, data collection and refinements, and the computer programs employed[14–20] are summarised in Table 1. For compound **3**, a data set collected using a CAD-4 diffractometer at room temperature provided the essential features of the structure, but the ratio of observations to parameters was very low. Accordingly a second data set was collected at low temperature using a Nonius Kappa-CCD diffractometer as described in Table 1.

For compound **2**, the orthorhombic space group *Pbcn* was uniquely assigned from the systematic absences: $0kl$ absent when $k=2n+1$, $h0l$ absent when $l=2n+1$, $hk0$ absent when $(h+k)=2n+1$. As well as the resorcinarene and two molecules of 4,4′-trimethylenedipyridine in general positions, the structure analysis also revealed methanol molecules disordered over two half-occupied equivalent sites related by a two-fold rotation axis parallel to [010]. Within one of the molecules of the dipyridine, the heterocyclic ring containing atom N71 was found to be disordered. The diffraction data were most satisfactorily fitted by a model which assigned to this ring two equally-populated sets of atom-sites, generated by rotation of the ring about the N71···C74 vector, such that the two ring-orientations are inclined at 35.7(4)° to one another. The orthorhombic space group *Pbca* was uniquely assigned for compound **3** from the systematic absences: $0kl$ absent when $k=2n+1$, $h0l$ absent when $l=2n+1$, $hk0$ absent when $h=2n+1$. The asymmetric unit contains one molecule each of the resorcinarene, 2,2′-bipyridyl and water, all in general positions and fully ordered, together with a disordered molecule of methanol. The water and the methanol molecules in **3** both participate in the hydrogen-bonding scheme: there is also a partially-occupied water site, with s.o.f. of 0.159(7), which is not involved in any close contacts with the rest of the structure. For both **2** and **3**, all the hydrogen atoms of the resorcinarene and the bipyridine components, as well as those of the water molecule and the hydroxy hydrogen in the methanol in **3**, were located from difference maps. All hydrogen atoms located in this way were included in the final refinements as riding atoms with O–H 0.820 Å and C–H in the range 0.93–0.98 Å. Supramolecular analysis of the refined structures was made with the aid of PLATON;[20] the figures were prepared with the aid of ORTEP-II[19] and PLATON.[20] Details of the hydrogen-bonding schemes are in Table 2 and 3. Fig. 1 and 3 show the asymmetric units of compounds **2** and **3** respectively, and Fig. 2, 4 and 5 illustrate aspects of the supramolecular architectures.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/115.

Results and discussion

Co-crystallisations

The C_{4v} isomer of *C*-methylcalix[4]resorcinarene, when co-crystallised with 4,4′-trimethylenedipyridine from solutions in methanol, provided the expected 1:2 adduct **2**, although solvated with one half a molecule of methanol per resorcinarene. The 1:2 stoichiometry was expected on the grounds that this isomer of the resorcinarene generally exhibits four intramolecular O–H···O hydrogen bonds,[12,21–23] and hence acts as a donor of only four intermolecular hydrogen bonds, while the 4,4′-trimethylenedipyridine acts as a double acceptor. However, 2,2′-bipyridyl was not expected to act as a simple bridging unit between pairs of resorcinarene molecules in the manner of 4,4′-bipyridyl[12] or 4,4′-trimethylenedipyridine, compound **2**, because of the closeness of the two nitrogen atoms and the likely orientation of the resulting O–H···N hydrogen bonds, regardless of the twist about the central C–C bond of this bipyridyl. Accordingly the observed 1:1 ratio in **3** was not unexpected.

The degree of solvation and guest-inclusion in the calixarene cavity is unpredictable and varies quite subtly with crystallisation conditions. Thus when *C*-methylcalix[4]resorcinarene was crystallised by dissolution in boiling pyridine, followed by cooling, a 1:6 adduct was produced in which four molecules of pyridine are hydrogen bonded to the resorcinarene, a fifth is included in the calixarene cavity and the sixth is outside the calixarene·(pyridine)$_4$ complex as solvent of crystallisation.[12] By contrast, crystallisation of the same calixarene from pyridine wholly at room temperature yielded just a 1:4 complex **4**; while structure determination for **4** has so far been precluded

Table 1 Experimental details

	Compound **2**	Compound **3**
Crystal data		
Chemical formula	$C_{58.5}H_{62}N_4O_{8.5}$	$C_{43}H_{46.32}N_2O_{10.16}$
Chemical formula weight	957.12	754.35
Cell setting	Orthorhombic	Orthorhombic
Space group	*Pbcn*	*Pbca*
a/Å	25.7972(4)	13.9906(4)
b/Å	16.5089(3)	17.8679(5)
c/Å	23.7612(4)	29.3316(7)
V/Å^3	10119.5(3)	7332.4(3)
Z	8	8
$F(000)$	4072	3199.2
D_x/Mg m^{-3}	1.256	1.367
D_m/Mg m^{-3}	not measured	not measured
Radiation type	Molybdenum Kα	Molybdenum Kα
Wavelength/Å	0.71073	0.71073
No. of reflections for cell parameters	10286	7408
θ range (°)	1.70–26.37	1.97–26.37
μ/mm^{-1}	0.084	0.098
Temperature/K	150(1)	150(1)
Crystal form	Block	Plate
Crystal size/mm	0.42 × 0.37 × 0.36	0.25 × 0.20 × 0.05
Crystal colour	Brownish-yellow	Brownish-yellow
Data collection		
Diffractometer	Kappa-CCD	Kappa-CCD
Data collection method	360 × 1° ϕ scans	360 × 1° ϕ scans
Absorption correction	none	none
No. of measured reflections	69128	42325
No. of independent reflections	10286	7408
No. of observed reflections	4980	4173
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.031	0.031
θ_{max} (°)	26.37	26.37
Range of h, k, l	$-32 \rightarrow h \rightarrow 32$ $-19 \rightarrow k \rightarrow 20$ $-29 \rightarrow l \rightarrow 29$	$-17 \rightarrow h \rightarrow 17$ $-22 \rightarrow k \rightarrow 22$ $-36 \rightarrow l \rightarrow 36$
Intensity decay (%)	no decay	no decay
Refinement		
Refinement on	F^2	F^2
$R[F^2 > \sigma(F^2)]$	0.0465	0.0505
$wR(F^2)$	0.1312	0.1433
S	0.865	0.916
No. of reflections used in refinement	10286	7408
No. of parameters used	671	505
H-atom treatment	constr	constr
k in $w = 1/[\sigma^2(F_o^2) + (kP)^2]$ $[P = (F_o^2 + 2F_c^2)/3]$	0.0712	0.0815
$(\Delta/\sigma)_{max}$	0.001	0.000
$\Delta\rho_{max}$/e Å^{-3}	0.312	0.649
$\Delta\rho_{min}$/e Å^{-3}	-0.347	-0.368
Extinction method	SHELXL	None
Extinction coefficient	0.00073(12)	—
Source of atomic scattering factors	International Tables for Crystallography (Vol. C)	
Computer programs		
Data collection	Kappa-CCD[a]	
Cell refinement	DENZO[b]	
Data reduction	DENZO	
Structure solution	SHELXS97[c]	
Structure refinement	NRCVAX96[d] and SHELXL97[e]	
Molecular graphics	NRCVAX96, ORTEP[f] and PLATON[g]	
Preparation of material for publication	NRCVAX96 and SHELXL97	

[a]Ref. 14. [b]Ref. 15. [c]Ref. 16. [d]Ref. 17. [e]Ref. 18. [f]Ref. 19. [g]Ref. 20.

by a lack of suitable crystals, the most plausible interpretation of the 1 : 4 stoichiometry is in terms of the hydrogen-bonded adduct previously observed,[12] but without the cavity-included and the solvating pyridine units. Similarly, co-crystallisation of *C*-methylcalix[4]resorcinarene with 4,4′-bipyridyl from acetonitrile solution yielded a 1 : 2 adduct, with acetonitrile trapped in the calixarene cavity;[12] use of methanol or ethanol as solvent, as here, produced again the 1 : 2 adduct, but now solvated not by either alcohol, but by three molecules of water per calixarene, compound **5**; the water in **5** has presumably been captured either from the solvent, or from the atmosphere during crystallisation. The extreme sensitivity of structure in these systems to the solvent employed for crystallisation is further illustrated by the resorcinarene itself, for which both aquated cubic (space group *I*432, $Z = 12$)[24] and butanone-solvated monoclinic (space group $P2_1$/m, $Z = 2$)[22] forms have been reported.

The supramolecular structure of 2

In compound **2**, the resorcinarene component forms four asymmetric intramolecular O–H···O hydrogen bonds (Fig. 1

and Table 2): the orientation of these hydrogen bonds is such as to reduce the overall symmetry of this component from C_{4v} to C_{2v}. There are thus four hydroxy groups available on each resorcinarene molecule in compound **2** for the formation of intermolecular O–H···N hydrogen bonds to the 4,4′-trimethylenedipyridine component: four of the eight oxygen atoms in the resorcinarene component thus act as both donor and acceptor of hard hydrogen bonds,[25] and the other four as donor only. The disordered methanol molecules, however, do not play any part in the hydrogen bonding in **2**: the oxygen atom forms no non-bonded contacts significantly shorter than the sum of the van der Waals radii with any of the other atoms in the structure. Oxygen atoms O13 and O15 form O–H···N hydrogen bonds with N51 and N71 respectively, within the asymmetric unit (Fig. 1 and Table 2), while atoms O33 and O35 at (*x*, *y*, *z*) form hydrogen bonds with N81 and N61 respectively in the neighbouring unit at (*x*, *y*, −1 +*z*). The basic supramolecular structure thus comprises a ribbon running parallel to the [001] direction and generated by translation: eight such ribbons run through the unit cell. This essentially flat ribbon propagated by translation may be compared with the highly-puckered zig-zag ribbon in the analogous adduct formed by the same resorcinarene with 4,4′-bipyridyl,[12] where the ribbon is propagated by the action of a two-fold screw axis.

The eight identical ribbons in the structure of compound **2** are connected together in pairs. The aliphatic spacer unit C57–C59 (Fig. 1 and 2) of the dipyridine at (*x*, *y*, *z*) fits across the rim of the resorcinarene bowl in the neighbouring ribbon, at (0.5−*x*, 1.5−*y*, 0.5+*z*), while the aliphatic spacer C57–C59 of this latter unit fits across the bowl at (*x*, *y*, 1+*z*) in the first ribbon. Thus pairs of ribbons, in this case related by the action of the 2_1 screw axis at (0.25, 0.75, *z*), are held closely together: aliphatic spacers in one ribbon are guests in the calixarene bowls of the neighbouring ribbon. Additional stabilisation of these inter-ribbon interactions arises from the precise alignment of a pair of aromatic C–H bonds in the dipyridine of one ribbon, acting as hydrogen-bond donors to a pair of oxygen atoms in the neighbouring ribbon. Thus atoms C53 and C65 in the dipyridine at (*x*, *y*, *z*), *i.e.* one carbon atom in each heteroaromatic ring of this dipyridine, act as hydrogen-

Table 2 Hydrogen-bond dimensions in compound **2**

Bond	D	H	A	D···A/Å	H···A/Å	D–H···A (°)
a	O23	H23	O15	2.749(2)	1.94	171
b	O25	H25	O33	2.721(2)	1.92	165
c	O43	H43	O35	2.753(2)	1.94	169
d	O45	H45	O13	2.838(2)	2.04	166
e	O13	H13	N51	2.738(2)	1.93	169
f	O15	H15	N71	2.614(2)	1.82	162
g	O33	H33	N81^a	2.639(2)	1.85	160
h	O35	H35	N61^a	2.734(2)	1.93	167
i	C53	H53	O43^b	3.397(3)	2.59	146
j	C65	H65	O45^b	3.399(3)	2.51	159

Symmetry codes: $^a x, y, -1+z$; $^b 0.5-x, 1.5-y, 0.5+z$.

Table 3 Hydrogen-bond dimensions in compound **3**

Bond	D	H	A	D···A/Å	H···A/Å	D–H···A (°)
a	O13	H13	O45	2.741(2)	1.94	166
b	O15	H15	O23	2.808(2)	2.04	155
c	O25	H25	O33	2.749(2)	1.94	169
d^a	O35	H35	O43	3.191(3)	2.56	134
e	O43	H43	O8	2.705(3)	1.90	166
f	O45	H45	O7	2.759(3)	1.97	162
g	O7	H7	N51	2.727(3)	1.64	167
h	O23	H23	O7^b	2.685(3)	1.89	164
i	O33	H33	N61^c	2.680(2)	1.88	165
j^a	O35	H35	O25^d	2.794(2)	2.22	128
k	O8	H81	O35^e	2.972(3)	2.05	144
l	O8	H82	O33^d	2.894(2)	1.94	138
m	C48	H48B	O13^f	3.127(3)	2.52	121
n	C66	H66	O25^c	3.310(3)	2.56	139

^{a}Hydrogen bonds *d* and *j* are part of a three-centre system with O43 and O25^d as the two acceptors: the angle O43···H35···O25^c is 94° and the sum of the three hydrogen-bond angles around H35 is thus 360°. Symmetry codes: $^b 0.5-x, -0.5+y, z$. $^c -x, -y, -z$. $^d -0.5-x, 0.5+y, z$. $^e 0.5+x, 0.5-y, -z$. $^f -0.5+x, y, 0.5-z$.

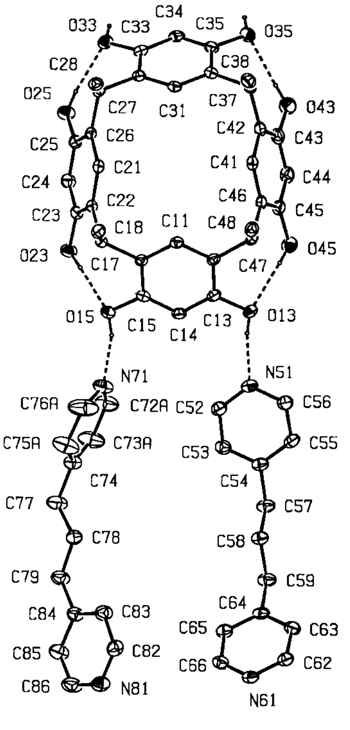


Fig. 1 The asymmetric unit in compound **2**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

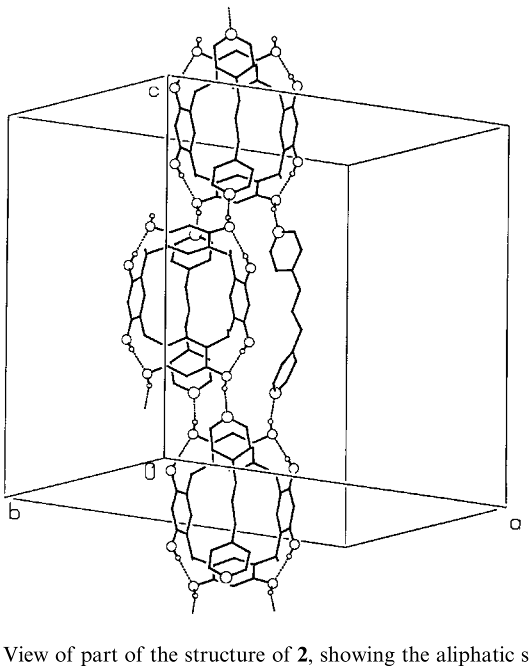


Fig. 2 View of part of the structure of **2**, showing the aliphatic spacer unit C57–C59 of one ribbon fitting across the resorcinarene bowl in the neighbouring ribbon.

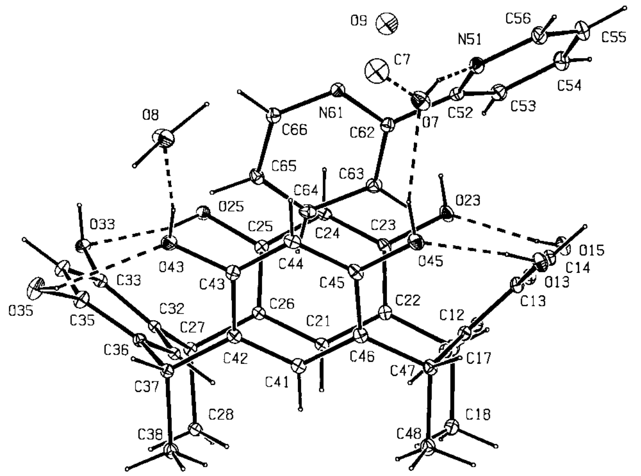


Fig. 3 The asymmetric unit of compound **3**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

bond donors to two atoms, O43 and O45 respectively, on the same aromatic ring of the resorcinarene at $(0.5-x,\ 1.5-y,\ 0.5+z)$. These C–H···O hydrogen bonds to the rim of the resorcinarene represent a form of intermolecular bonding, soft hydrogen bonds with oxygen as acceptor, which has not hitherto been widely recognised or exploited in this area.

Supramolecular structure of 3

The asymmetric unit of compound **3** contains one molecule each of the resorcinarene, 2,2′-bipyridyl, water and methanol (Fig. 3): all four components participate in the formation of hard hydrogen bonds. The resorcinarene forms four intramolecular O–H···O hydrogen bonds, arranged not in the usual C_{2v} configuration, but with only C_1 symmetry (Fig. 3 and Table 3). The other four hydroxy groups, associated with O23, O33, O43 and O45, all form hydrogen bonds with other components of the structure: O23 and O45 form O–H···O bonds with methanol molecules, O33 with a bipyridyl molecule, and O43 with a water molecule; in addition, atom O35 by forming a bifurcated (three-centre) hydrogen bond is linked also to another resorcinarene molecule. Hence each resorcinarene acts as a quintuple donor of hydrogen bonds to, and as a triple acceptor from, other molecules. The methanol molecule acts both as hydrogen-bond donor, to a bipyridyl, and as a double acceptor, from two different resorcinarene molecules. The water molecule acts as a single acceptor from one resorcinarene and as donor to two others. Finally, the bipyridyl molecule acts as a double acceptor in O–H···N hydrogen bonds, where the two donors are methanol and a resorcinarene molecule. Within the asymmetric unit (Fig. 3) atoms O43 and O45 act as donors to water and methanol respectively; methanol in turn acts as donor to atom N51 of the bipyridyl, while the other ring of the bipyridyl (N61 and C62–C66) lies over the rim of the calixarene. The hydrogen bonding is thus much more complex in compound **3** than in compound **2**.

The overall supramolecular structure of compound **3** consists of paired two-dimensional rhomboidal nets generated solely by intermolecular O–H···O hydrogen bonds. These nets are aligned so that pairs of calixarenes, which lie across centres of inversion with their hydroxylic rims close to one another, generate large cavities in which pairs of 2,2′-bipyridyl molecules are held (Fig. 4 and 5). Such a pair of nets utilises only half the contents of the unit cell and there are two such paired nets, one lying in the domain $-0.27<z<+0.27$ and the other in the domain $+0.23<z<+0.77$. Between the independent pairs, there are no contacts which are significantly shorter than the sum of the van der Waals radii.

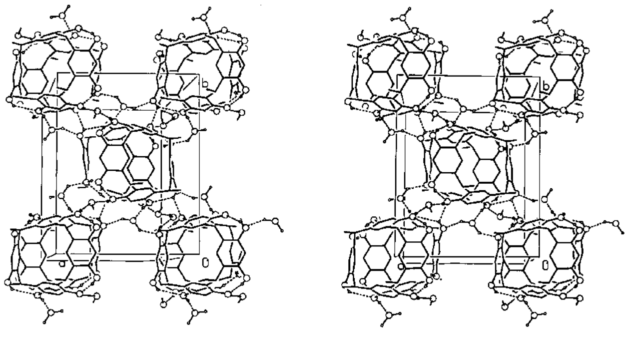


Fig. 4 Stereoview of part of the structure of **3**, showing one of the two-dimensional nets generated solely by O–H···O hydrogen bonds with the centrosymmetric pairs of resorcinarene bowls.

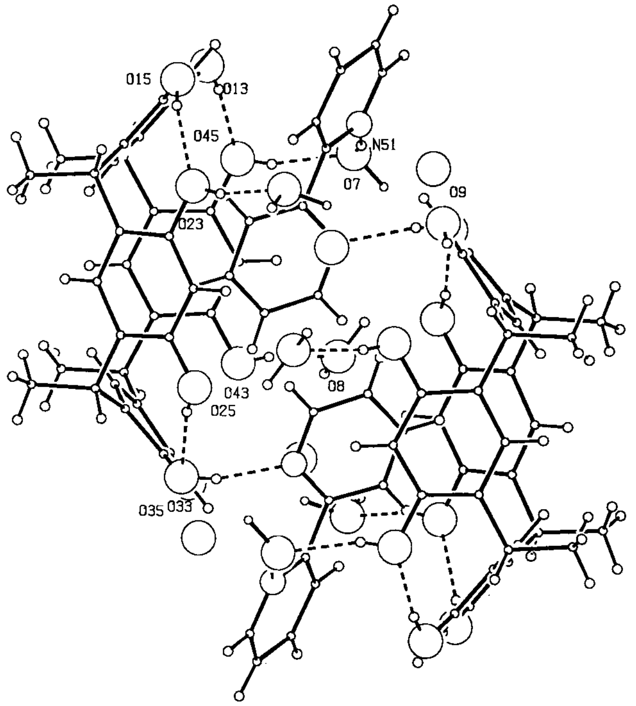


Fig. 5 View of part of the structure of **3**, showing the placing of pairs of 2,2′-bipyridyl molecules within the cavity formed by a pair of resorcinarene molecules.

Hydrogen-bonding motifs

All of the four independent intramolecular O–H···O hydrogen bonds in compound **2**, labelled *a*–*d* in Table 2, form cyclic motifs, whose graph set descriptor is $S(8)$,[1,2] while each of the O–H···N and C–H···O hydrogen bonds, *e*–*h* and *i* and *j* respectively in Table 2, is of type D. For the hard hydrogen bonds, O–H···O and O–H···N, it is necessary to consider four-fold combinations of independent hydrogen bonds in order to describe the overall supramolecular structure (Fig. 1 and 2). The combination of the four O–H···O hydrogen bonds *a*–*d* gives $N_4=R_4^4(24)$, while the combination of the four independent O–H···N hydrogen bonds *e*–*h* gives $N_4=R_4^4(36)$. There are also two independent combinations of O–H···O and O–H···N hydrogen bonds, defining the two edges of the ribbon: each of $(a+b+f+g)$ and $(c+d+e+h)$ gives $N_4=C_4^4(22)$. The inter-ribbon soft C–H···O hydrogen bonds, *i* and *j*, combine to give a cyclic motif with $N_2=R_2^2(14)$.

In compound **3**, the water molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor, *via* H81 (Table 3), to atom O35 of the resorcinarene molecule at $(0.5+x, 0.5-y, -z)$, while the water molecule at $(0.5+x, 0.5-y, -z)$ in turn acts as donor *via* H81 to atom O35 at $(1+x, y, z)$. Propagation of this interaction thus produces a continuous chain running parallel to [100] and generated by the action of a two-fold screw axis: this chain, built up from hydrogen bonds *d*, *e* and *k* in Table 3, is thus a spiral and has graph-set descriptor $N_3 = C_3^3(6)$. The same water molecule at (*x*, *y*, *z*) also acts as hydrogen-bond donor, this time *via* H82, to atom O33 of the resorcinarene at $(-0.5-x, 0.5+y, z)$, and the water at $(-0.5-x, 0.5+y, z)$ in turn acts as donor to atom O33 at $(x, 1+y, z)$. Propagation of this hydrogen-bond sequence (hydrogen bonds *d*, *e* and *l* of Table 3) produces a zig-zag chain with $N_3 = C_3^3(10)$, generated by the glide plane and running parallel to [010]. The interaction of these two chain motifs generates a two-dimensional, rhomboidal network parallel to the (001) plane. Each chain utilises just one O–H bond of the water molecules, O–H81 in the [100] direction and O–H82 in the O–H82 direction, so that the intermediate water molecules in each chain still have hydrogen-bonding capacity to be accounted for. The intermediate water molecule in the [100] chain, at $(0.5+x, 0.5-y, -z)$ acts as donor *via* H82 to atom O33 in the resorcinarene at $(-x, -y, -z)$: similarly, an intermediate water molecule in the [010] chain, at $(0.5-x, -0.5+y, z)$ acts as donor *via* H81 to atom O35 in the same resorcinarene molecule at $(-x, -y, -z)$. Hence the hydrogen-bonding role of the water molecules is two-fold: firstly, they generate the two sets of chains parallel to [100] and [010] and hence the resulting two-dimensional network; secondly, they link together pairs of such parallel networks related by the action of centres of inversion.

The arrangement of the two linked nets is such that pairs of resorcinarenes lie across centres of inversion. The two calixarene bowls point towards each other but the local (approximately four-fold) rotation axes of the resorcinarenes are offset by *ca.* 2.9 Å. Together with the associated water and methanol molecules, these pairs of resorcinarenes produce a large cavity in which two molecules of 2,2′-bipyridyl are held by a combination of O–H···N and C–H···O hydrogen bonds (Fig. 5). The combination of the O–H···O hydrogen bonds *a*, *b*, *c* and *f* at the equator of the cavity and the O–H···N hydrogen bonds *g* and *i* holding the bipyridyl molecules in the cavity, generates a cyclic $R_{12}^{12}(46)$ motif.

In effect, the supramolecular structure of **3** has formed by self-assembly of a network of hydrogen-bonded carcerands, each cavity in which is constructed from two resorcinarenes, analogous to covalently-linked carcerands.[13,26] Calixarene dimers, having much more open structures with the two components linked together by eight molecules of either propan-2-ol[27] or water,[28] have recently been reported, but in both cases the dimers were isolated rather than joined into a continuous connected network, as in compound **3**. The formation of isolated dimers can be associated, in the one case[27] with external C_{60} fullerene units, one per dimer, which prevent any hydrogen-bonded connections between the dimers and, in the other,[28] with an interior $[NEt_4]^+$ cation assisting the stability of the system by means of cation···π(arene) interactions.

Molecular conformations and dimensions

The overall shape of the *rccc* isomer of a *C*-alkylcalix[4]resorcinarene is largely controlled by the conformational requirements of the 16-membered carbocycle forming the base of the calixarene, in which four distinct five-carbon fragments are constrained to be planar or nearly so, although these requirements are, of course, moderated by the strength and orientation of the intra- and inter-molecular hydrogen bonds formed by the hydroxy groups around the rim, in particular those involving guest species within the calixarene bowl. The shape of the calixarene bowl is most simply described in terms of the angles made by each of the aromatic rings *Cnm* ($n=1$–4; $m=1$–6) with a reference plane, conveniently chosen as the plane defined by the atoms *Cn7* ($n=1$–4). In both compounds **2** and **3** these angles are alternately *ca.* 40° and *ca.* 65°, showing that the skeletal conformation is, in each case, much closer to C_{2v} symmetry than to the idealised C_{4v}. A complementary measure of the deviation of the bowl from idealised symmetry is provided by the O···O distances in the intramolecular O–H···O hydrogen bonds (Table 2 and 3).

There are two independent molecules of 4,4′-trimethylenedipyridine in compound **2**: in both, the central aliphatic spacer unit is in the fully-extended all-*trans* conformation. 4,4′-Trimethylenedipyridine itself does not appear in the Cambridge Structural Database,[29] but the bond lengths and angles found here in compound **2** are unexceptional. In compound **3**, the two pyridyl rings are inclined to one another at an angle of 40.4(1)°: the N···N bite distance, 2.806(3) Å, is thus rather larger than the 2.69 Å expected for a planar 2,2′-bipyridyl component.

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